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Compound Formation in Phenol- Cresol Mixtures

DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIRE-
MENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE FACULTY OF PURE SCIENCE IN
COLUMBIA UNIVERSITY

BY

JACOB J. BEAVER, B.S., M.A.

New York City

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W. J. S.

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ACKNOWLEDGMENT

The author wishes to thank Professor James Kendall, at whose suggestion this problem was undertaken, for his generous and helpful advice and to express his appreciation of him both as a friend and as a teacher.

The author also desires to thank the other members of the chemistry department of Columbia University for the many courtesies extended to him.

COMPOUND FORMATION IN PHENOL-CRESOL MIXTURES

1. What was attempted?

(1) The attempt was made to harmonize the results for phenol-cresol mixtures with the general rules previously formulated with respect to addition compound formation in two component systems. The six binary systems formed by phenol and the three cresols were examined by means of conductivity, viscosity and freezing-point depression measurements.

2. In how far were the attempts successful?

(2) It has been shown that, in the systems studied, the complexes formed are of the nature of *substitution* compounds (rather than *addition* compounds) of which the average molecular complexity, as demonstrated by the specific conductivity, viscosity and freezing-point depression results, is not greatly different from the pure components. Under this view the observed experimental results fall into line with the general theory of compound formation.

3. What contribution actually new to the science of chemistry has been made?

(3a) New standards of purity have been established and more accurate determinations of their chief physical constants made for phenol and the cresols.

(3b) New and exact measurements of the specific conductivities and viscosities of the six binary systems formed by phenol and the cresols have been made. The freezing-point depression curves for the pure components and various binary mixtures in benzene solution have also been constructed.

(3c) Additional confirmation has been given to a previously formulated and generalized theory of compound formation.

COMPOUND FORMATION IN PHENOL-CRESOL MIXTURES.

In a series of communications in the past few years¹ addition compound formation in a large number of binary systems has been investigated, particular attention being paid to variations in the extent of compound formation as the constituent radicals of the components were varied. In all more than 100 new compounds have been isolated and simple and definite rules regarding the relative stability of addition compounds in solutions have been derived. It has been shown that the extent of addition compound formation in binary mixtures is controlled primarily by the "chemical contrast," with the stability of complexes increasing uniformly with the differences in character (i.e., the positive or negative nature of the constituent groups) of the two compounds.

In the course of the work, however, it was noted that the results obtained with phenols were abnormal. For example, it was found² that phenol and the three cresols gave more stable compounds with the basic substance, dimethylyprone, than did dinitrophenol or even picric acid, both of which substances are more acidic than the phenols. It was further found³ that weak acids, although of far greater acidic strength than the phenols (as shown by the dissociation constants), give the more stable compounds with trichloroacetic acid. To explain this discrepancy a tentative explanation, postulating the existence of phenols in two tautomeric forms of widely different acidic strengths, was proposed.¹

Recently, Dawson and Mountford² have made a thorough investigation of compound formation in systems of the type phenol-cresol by the freezing-point method. They found that of the six binary systems possible, five give evidence of compound formation, while the sixth (phenol—o-cresol) exhibits formation of solid solutions. This result they considered as rather remarkable in view of the close chemical similarity of the components and concluded that

¹Kendall, J.A.C.S., *36*, 1222, 1722 (1914); *38*, 1309 (1906); Kendall and Carpenter Ibid., *36*, 248 9 (1914); Kendall and Booge, Ibid., *38*, 1712 (1916); *39*, 2323 (1917); Kendall, Booge and Andrews, Ibid., *39*, 2303 (1917).
.....

²Kendall J.A.C.S., *36*, 1222 (1910).

³Kendall, Ibid., *38*, 1317 (1916).

¹Kendall, Booge and Andrews, J.A.C.S., *39*, 2306 (1917).

²Jour. Chem. Soc., *113*, 923 (1918).

"the relations disclosed by the freezing-point diagrams are consequently not in accord with what would have been anticipated on the basis of the views advocated by Kendall." The fact that the uniform abnormality of the phenols had already been emphasized was apparently overlooked.

A similar study of phenol-cresol systems by Fox and Barker³ gave widely different results, a stable compound (phenol—m-cresol) being isolated in only one of the six binary systems examined. Four of the systems show eutectic points at approximately 50 molecular per cent of the components while the remaining system o-cresol—m-cresol gives two eutectic points with no well-defined maximum between them. These discrepancies are in all probability due to the inadequate purification of the materials employed by Fox and Barker and to the general inferiority of their method. In view of the greater care exercised by Dawson and Mountford in all the details of their work, there is no reason to doubt the accuracy of their experimental data.

In order to obtain more experimental data as to the nature of the compounds indicated by Dawson and Mountford, and in the hope of bringing the results for systems containing phenols into line with the rest of the previous work, these six systems have been subjected to additional examination.

CONDUCTIVITY MEASUREMENTS

Kendall and Gross¹ have shown the validity of the general rule that compound formation and ionization in solutions proceed in parallel. For a series of binary organic mixtures it has been established experimentally that an increase in compound formation is regularly accompanied by a similar increase in specific conductivity. Where the extent of compound formation was known to be very small (as shown by freezing-point curves of the systems), the conductivity was practically zero; as compound formation increased in amount the conductivity became measurable; where combination was extensive, the conductivity was very markedly increased, being in some cases over one hundred times that of the higher component.

With these facts in mind it was decided that the first line of attack in the present work was to be the determination of the specific

³J. Soc. Chem. Ind., 37, 268 (1918).

¹J.A.C.S., 43, (1921).

conductivity-composition curves of the phenol-cresol mixtures. As the conductivities to be measured were equal to, or below, the order of pure water (5.5×10^{-8} at $25^{\circ}\text{C}.$) it was necessary to have a cell with a much larger electrode surface than any available in order to obtain the required degree of accuracy in the experimental results. The problem was further complicated by the necessity of having the cell as small as possible so that only the minimum amount of substance would be used.

To fulfil these requirements a cell was constructed using the design described by Beans and Eastlack¹ but having six concentric platinum cylinders for the electrodes instead of two as used by them. The electrodes were $2\frac{1}{2}$ cm. high with the smallest cylinder 1 cm. in diameter and the others increasing in diameter in steps of two millimeters which gives the outer cylinder a diameter of 2 cm. Alternate cylinders were connected to heavy platinum wires sealed into the supporting tubes. The cylinders are separated by small glass beads attached to thin glass rods running through holes at both top and bottom of the cylinders. There are three equally spaced (i.e., at intervals of 120°) rods at both ends of the cylinders. The three lower rods are bent downward and continued so that they can be sealed into the bottom of the cell. This method of holding the electrodes in place is different from that used by Beans and Eastlack but was found to be necessary in order to hold the cylinders rigidly in place. This rigidity is a necessity if a permanent value for the cell constant is desired. That this end was attained is shown by the following results for the value of the cell constant: at the beginning of the work it was 0.001426; six months later it was 0.001427, a change of only 0.07 per cent (in each case the results are the average of ten determinations). With this cell all the solutions, with the exception of o-cresol, gave a resistance of less than 100,000 ohms, and no difficulty was experienced in obtaining distinct minima. Platinized electrodes could not be used, since in the presence of platinum black phenol-cresol mixtures turn yellow, with a measurable increase in conductivity. Taylor and Acree² show that if the electrodes are sand blasted to insure a rough surface, the conductivities obtained with unplatinized are not measurably different from those obtained with platinized electrodes. The electrodes used in the above cell were accordingly sand-blasted, and in that con-

¹J.A.C.S., 37, 2674 (1915).

²J.A.C.S., 38, 2396 (1916).

dition exerted no action on the solutions but gave perfectly definite and consistent readings.

The bridge employed was a 4.7 meter circular slide wire instrument, well grounded and carefully calibrated. The resistance coils up to 1000 ohms were bifilar wound; those over 1000 ohms were of the Curtis type which have practically no inductance or capacity when using a 1000 cycle alternating current. The capacity of the cell was balanced out by means of rotary air condenser connected in parallel with the resistance coils. The source of current was a Vreeland oscillator producing a pure sine wave alternating current of 1000 cycles per second. A high resistance telephone receiver was used to determine the balance point.

Most of the measurements were carried out in a large Freas thermostat, regulated to $25^{\circ} \pm 0.005^{\circ}$. The absolute temperature was taken from a thermometer graduated in hundredths of a degree and standardized at the Bureau of Standards. Many of the solutions which have a higher freezing-point than 25° could be super-cooled sufficiently to enable direct determinations at this temperature to be made. With phenol and mixtures very rich in phenol, however, solidification could not be prevented in the presence of the sand-blasted electrodes, although viscosity measurements at 25° could be made. To complete the specific conductivity curves for phenol-cresol mixtures at 25° it was therefore necessary to perform experiments for these concentrations at higher temperatures and extrapolate the results.¹ For this purpose two smaller thermostats, regulated to $40^{\circ} \pm 0.05^{\circ}$ and $50^{\circ} \pm 0.10^{\circ}$ respectively, were fitted up. Linear extrapolation was assumed to be valid over the small temperature range involved. While this assumption is probably not strictly accurate the values so obtained show very good agreement with the direct measurements at 25° , as may be seen by referring to curves 4, 5, 6 in figure I. In this diagram, the extrapolated sections of the different curves are indicated by broken lines.

Mixtures were made up by direct weighing with the use of a Lunge pipet. The compositions as given in the tables below are accurate to within ± 0.05 per cent. The specific conductivity values are *relatively* of the order of 0.1 per cent but no claim is made for this accuracy in the *absolute* values. This is due to inductance and capacity effects between the apparatus and earth, when large resist-

¹Compare Kendal and Gross, loc. cit., p. . .

ances are measured by the use of a high frequency alternating current.

PURIFICATION OF MATERIALS

As in the work of Kendall and Gross it was found that the presence of impurities in quantities insufficient to exert a measurable effect on the freezing-point or boiling-point caused a very considerable change in specific conductivity. A constant value for specific conductivity was therefore made the final criterion of purity.

The method of purification was essentially the same in each case. The purest material obtainable was repeatedly fractionated from special stills made of Pyrex glass. The stills were so constructed that the hot vapors came in contact with nothing but glass, thus eliminating the possibility of contamination from the cork. A middle fraction of constant freezing-point usually gave a product of constant specific conductivity after 3 to 6 additional fractionations.¹ In view of the hygroscopic nature of the materials used and of the marked influence exerted by traces of water upon their specific conductivity, measurements were restricted to cold dry days. The sensitivity of the materials toward moisture constitutes the chief source of error in the whole of the experimental work and all possible precautions were taken to eliminate its effect upon the results.

THE SYSTEM: PHENOL—O-CRESOL

A c.p. sample of phenol, after about twenty fractional distillations using only the middle fraction in each succeeding distillation, gave a final product of specific conductivity 11.98×10^{-8} at 40° and 14.07×10^{-8} at 50° .¹ The only previously recorded value is that of Riesenfeld; 43×10^{-8} at 43° .² The freezing-point of this sample was $39.70 \pm 0.02^\circ$ using a standardized thermometer. This is identical with that found by Morgan and Egloff³ for a specially prepared and purified sample of phenol. Several investigators have reported considerably higher values for phenol,⁴ which seems to indicate that

¹It was found that the addition of 0.2 grams of anhydrous sodium carbonate to 100 grams of phenol hastened the elimination of impurities.

²The fact that twenty fractionations were required to purify the material shows how difficult it is to remove the last traces of impurities. On the average 100 grams of purified material was obtained from 1000 grams of the crude material.

³Riesenfeld, *Z. physik. Chem.*, **41**, 346 (1902).

⁴*J.A.C.S.*, **38**, 844 (1916).

⁵ 42.4° was found for a Kahlbaum sample (Kendall and Carpenter, *J.A.C.S.*, **36**, 2498 (1914)).

the commercial product is apt to contain some impurity which *raises* its freezing-point. The original material here employed gave a slightly higher freezing-point than that of the final product.

Pure o-cresol was obtained from a c.p. product by similar continued fractionation, the final material possessing a specific conductivity of 0.127×10^{-8} at 25° and a freezing-point of $30.60 \pm 0.02^\circ$. No previous measurements of the conductivity are recorded; for the freezing-point the highest recorded value is 30.45° .¹

The data for this system are given below in Table 1. The compositions of the solutions are expressed in molecular per cent throughout. The specific conductivities are in reciprocal ohms $\times 10^8$ at 25° except as noted above. The viscosity data which are added will be discussed later.

TABLE I
PHENOL - O-CRESOL

Mol. % Phenol	Spec. Cond. $\times 10^8$	Viscosity
0.0	0.127	0.07608
13.43	0.375	0.07835
19.73	0.415	0.07930
30.00	0.612	0.08099
38.81	0.693	0.08235
49.10	0.885	0.08404
62.83	1.686	0.08565
69.27	2.583	0.08645
75.79	3.321	0.08731
80.03	4.196	0.08757
87.30	5.422	0.08825
90.10	6.183	0.08851
100.00	8.84	0.08945

THE SYSTEM: PHENOL—M-CRESOL

Pure m-cresol was prepared by repeated fractionation of a c.p. sample. The effect of the distillation over sodium carbonate in lowering the specific conductivity was very marked in the case of this substance. The specific conductivity of the final product was 1.397×10^{-8} at 25° ; its freezing-point was $11.10 \pm 0.02^\circ$. The freezing-point as reported¹ is 10.9° ; no conductivity measurements could be found.

¹Dawson and Mountford, loc. cit.

¹Kendall, J.A.C.S., 38, 1315 (1916). Dawson and Mountford employed a product freezing at 10.0° ; Fox and Barker used material with a much lower freezing-point, their material apparently containing about 15 per cent. p-cresol. (See Dawson and Mountford, loc. cit., p. 924).

TABLE II
PHENOL - M-CRESOL

Mol. % Cresol	Spec. Cond. $\times 10^8$	Viscosity
0.0	8.84	0.08945
6.99	7.431	0.09105
10.79	6.810	0.09206
18.10	5.923	0.09398
26.75	5.094	0.09698
36.48	4.197	0.09961
48.26	3.379	0.1040
54.98	2.988	0.1070
61.52	2.587	0.1095
68.63	2.175	0.1131
75.51	1.887	0.1169
87.41	1.592	0.1250
100.00	1.397	0.1342

THE SYSTEM: PHENOL—P-CRESOL

The preparation of pure p-cresol from several presumed c.p. samples was unsuccessfully attempted, the elimination of traces of m-cresol (which possess almost exactly the same boiling-point)¹ not being possible. To obtain pure p-cresol pure p-toluidine (F.P. 43.0°) was diazotized in 6 molar hydrochloric acid solution by slow addition of the theoretical amount of sodium nitrite, the temperature being maintained below 10° and thorough mixture secured by vigorous stirring. When the reaction was complete, the temperature was gradually raised to 40° and the solution allowed to stand over night. It was then steam distilled, the distillate extracted with ether, dried and fractionated as described above. The specific conductivity of the material used was 1.378×10^{-8} at 25°; it gave a freezing-point of $34.55 \pm 0.02^\circ$. Practically the same freezing-point was obtained by Kendall and Carpenter² and Kendall³; while the material used by Dawson and Mountford possessed a freezing-point of 34.15°. No previous determination of specific conductivities are recorded in the literature.

It was found that no matter how carefully the para isomer was purified it turned yellow in the course of a day if exposed to sunlight. The other pure substances when purified as outlined above would show no appreciable color at the end of a month. As there

¹The b.p. (under 760 mm. pressure) of m-cresol is 202.1°, of p-cresol 202.5°. In the cases of phenol and p-cresol or phenol and o-cresol the differences in b.p. are sufficient to permit of their separation by fractionation. (See Dawson and Mountford, loc. cit., p. 937).

²Kendall and Carpenter, loc. cit.

³Kendall, J.A.C.S., 38, 1315 (1916).

was no detectable impurity present it is probable that the para compound is considerably more sensitive to light than its homologues. The data presented below in Table III were obtained with the use of freshly-prepared material.

TABLE III
PHENOL - P-CRESOL

Mol. % Cresol	Spec. Cond. x 10 ⁸	Viscosity
0.0	8.84	0.08945
12.17	7.151	0.09463
24.13	5.863	0.09835
36.15	4.972	0.1042
47.82	4.201	0.1099
61.49	3.423	0.1175
68.09	3.012	0.1218
84.02	2.210	0.1327
100.00	1.378	0.1474

SYSTEMS CONTAINING TWO CRESOLS

In Tables IV, V and VI below, the conductivity and viscosity results for the binary cresol mixtures are given.

TABLE IV
O-CRESOL - M-CRESOL

Mol. % meta	Spec. Cond. x 10 ⁸	Viscosity
0.0	0.127	0.07608
11.97	0.178	0.08086
23.92	0.184	0.08582
36.29	0.362	0.09208
49.40	0.633	0.09939
60.46	0.767	0.1050
64.64	0.874	0.1075
69.39	0.977	0.1109
84.63	1.134	0.1216
100.00	1.397	0.1342

TABLE V
O-CRESOL - P-CRESOL

Mol. % para	Spec. Cond. x 10 ⁸	Viscosity
0.0	0.127	0.07608
12.50	0.188	0.08209
24.27	0.190	0.08854
36.96	0.344	0.09612
47.44	0.410	0.1030
57.67	0.507	0.1103
64.75	0.553	0.1163
70.91	0.601	0.1200
84.53	0.726	0.1327
100.00	1.378	0.1474

TABLE VI
M-CRESOL - P-CRESOL

Mol. % para	Spec. Cond. x 10 ⁸	Viscosity
0.0	1.397	0.1343
8.65	1.384	0.1346
17.33	1.378	0.1352
26.27	1.442	0.1360
29.29	1.449	0.1361
32.67	1.512	0.1369
37.62	1.551	0.1373
44.79	1.583	0.1385
51.77	1.567	0.1393
54.80	1.560	0.1401
69.97	1.728	0.1425
75.39	1.603	0.1432
86.12	1.495	0.1450
100.00	1.378	0.1474

The specific conductivity results given in the above tables are represented graphically in Figure I. Curves I, II, III show the data for the binary cresol systems, curves IV, V, VI the data for mixtures of phenol with cresols.

It is quite evident from inspection of this diagram that the specific conductivities of all the solutions examined are very little different from those of the pure components. This type of curve, according to the work of Kendall and Gross,¹ is characteristic of all mixtures in which the two components are essentially similar in character. In such mixtures little or no increase in molecular complexity through compound formation is to be expected. Hence the observed conductivity of such solutions should not differ to a marked extent (if the parallelism between molecular complexity and ionization is accepted) from that obtained by linear extrapolation from the specific conductivities of its constituents.

The conductivity results obtained are therefore in apparent contradiction with the freezing-point results of Dawson and Mountford, and in agreement with the generalization previously formulated by Kendall and quoted above. (p. 1.)

This discrepancy will be discussed more fully below, after the work on two other physical properties of phenol-cresol mixtures has been described. The investigation of the viscosity-composition curves of these systems was chosen as the second line of attack because of the marked effect of changes in molecular complexity upon the viscosity.

VISCOSITY MEASUREMENTS

In general viscosity curves for binary liquid mixtures fall into three distinct types.² The ideal curve, given by solutions in which no interactions at all take place on mixture is not linear but appreciably sagged. Where compound formation occurs in the mixtures, the viscosity is abnormally high; if compound formation is extensive the curve may even exhibit a *maximum*. These results are in harmony with the definition of viscosity as "essentially fractional resistance encountered by molecules of a solution moving over one another"³ and with the observed experimental facts as to the increase of viscosity with increasing molecular weight in a homologous series.¹ Where dissociation of an associated component takes place on admixture, the viscosity (owing to the production of smaller molecules) is abnormally low; if the dissociation is extensive the curve may even exhibit a *minimum*. In certain cases both com-

¹Kendall and Gross, *loc. cit.*, p. . .

²See Kendall and Munroe, *J.A.C.S.*, 43, 115 (1921).

³Kendall, *Medd. K. Vetén. Nobelinst.*, 2, No. 25 (1913).

pound formation and dissociation effects may be existent reproducing a curve quite similar to the ideal type.² A brief consideration of the chemical character of the components will be sufficient to enable one to distinguish such a system from one which is truly ideal. Usually, however, one effect will predominate sufficiently to give a curve quite distinct from the normal type.

It was hoped, therefore, that a study of the viscosity curves of phenol-cresol systems would either make possible a decision between the apparently conflicting conclusions drawn from freezing-point and conductivity measurements, or indicate the true conclusions.

The apparatus used for the determination of viscosities was of the Bingham type³, the experimental procedure being essentially the same as described by Kendall and Monroe.⁴ The tubes used were calibrated by means of pure m-cresol whose absolute viscosity in C.G.S. units was obtained from another tube previously standardized by means of conductivity water. The viscosity value for water was taken as 0.008946. Using this value the constants for the tube are obtained from the complete viscosity formula:

$$\eta = \frac{\pi g r^4 \rho t}{8 V l} - \frac{1.12 n P V}{8 \pi t l}.$$

(g =acceleration due to gravity; r =radius of the capillary; V =transpiration volume; l =total length of capillary; n =number of capillaries; P =density of the liquid), which reduces to the form

$$\eta = C \rho t - \frac{C' P}{t}$$

where C and C' are the constants of the tube.

The relative accuracy of the viscosity data given in Tables I to VI above is ± 0.2 per cent. With the apparatus employed a somewhat higher precision is attainable for most substances, but the temperature coefficient of viscosity of the substances employed is extremely high—approximately 10 per cent per degree.¹ Accurate density values are not essential for the exact determination of viscosity with the Bingham type of instrument since the density enters

¹Dunstan and Thole, "The Viscosity of Liquids," p. 15.

²Compare Kendall and Brakeley, J.A.C.S., 43, (1921).

³Bingham J. Ind. Eng. Chem., 6, 233 (1914); Bingham, Schlesinger and Coleman, J.A.C.S., 38, 27 (1916).

⁴Kendall and Monroe, J.A.C.S., 39, 1787 (1917).

¹Bramley, loc. cit., p. 10.

into the working formula only in the kinetic energy correction-factor which is approximately 1 per cent of the total. Consequently, after it had been found for each system that the density of an approximately equimolecular mixture was, within error limits, identical with the density found by linear interpolation from the specific volume-weight composition curves, no other density values were determined.²

The viscosity results for the six systems are reproduced in graphic form in the accompanying diagram (Figure II). Inspection of these curves shows that they are all very near to the ideal type.

When it is remembered, however, that we have independent evidence from other physical properties³ that phenol and the cresols are highly associated liquids it follows that this approximation to the normal type of curve must be due to the mutual result of the

²This assumption is in agreement with the actual density determinations carried out by Fox and Barker [J. Soc. Chem. Ind., 36, 845 (1917)] with less pure materials.

³See Turner, "Molecular Association"; also data given later.

two opposing effects discussed above—compound formation and dissociation. It appears that neither effect is predominant here, combination between the components being practically counterbalanced by mutual depolymerization, leaving the average molecular complexity essentially unchanged.

To obtain confirmation of this point of view, the molecular weights of the pure substances, and the average molecular weights of their binary mixtures, were determined in an inert solvent.

MOLECULAR WEIGHT DETERMINATIONS

The freezing-point of a pure liquid, on addition of an ideal solute, will be depressed according to the equation:¹

$$l_n x = (-Q/RT_o) \cdot (\Delta T/T)$$

(where x is the molecular fraction of solvent in the solution; Q the molecular heat of fusion of the solvent; T_o and T the absolute freezing-points of the pure solvent and the solution respectively; ΔT the freezing-point depression; and R 1.9852). If the solute is not ideal but associated, its average molecular weight in any solution of known composition can be calculated from the above equation by substituting the experimentally determined value for T and solving for x .

Benzene was selected as a suitable ideal solvent. The ideal freezing-point depression curve for this liquid has been given in a previous article.² The benzene used in the present work was dried over sodium and carefully fractionated from the same substance. The fraction used distilled between 80.2°—80.3°. (corr.)

To determine the freezing-point depression of benzene on addition of phenol and the cresols the standard Beckmann apparatus and method were employed using a thermometer calibrated at the Bureau of Standards. Undercooling was limited to 0.1° to 0.2°. For the depressions tabulated in Table VII the accuracy claimed is 0.01°. The "compound mixtures" were obtained by weighing somewhere near the approximate amounts of the two components into a small flask and then adding small amount of one of the components until the desired composition was obtained. In all cases the molecular composition is within 0.1 per cent of the theoretical molecular composition of the compound.

¹Roozeboom, "Heterogene Gleichgewichte", 2, 273 (1904).

²Kendall and Monroe, J.A.C.S., 43, 115 (1921).

TABLE VII

FREEZING-POINT DEPRESSION DATA

Phenol		Ortho-Cresol	
Mol. % Solute	ΔT	Mol. % o-cresol	ΔT
0.97	0.398°	0.88	0.591°
1.81	0.711°	1.86	1.170°
3.17	1.190°	2.84	1.752°
4.50	1.621°	3.81	2.257°
6.38	2.221°	4.71	2.728°
7.92	2.635°	5.95	3.341°
		7.53	4.082°
Meta-Cresol		Para-Cresol	
Mol. % m-cresol	ΔT	Mol. % para	ΔT
0.67	0.434°	0.95	0.590°
1.54	0.925°	2.01	1.180°
2.00	1.161°	3.18	1.691°
3.10	1.711°	4.54	2.225°
4.33	2.161°	5.70	2.625°
5.43	2.584°	7.10	3.102°
6.01	2.843°	8.68	3.569°
7.72	3.424°	10.33	4.065°
1 Phenol: 2 m-Cresol		1 Phenol: 1 o-Cresol	
33.33 mol. % : 66.67 mol. %		49.90 mol. % : 50.10 mol. %	
Mol.% compound	ΔT	Mol.% compound	ΔT
0.66	0.380°	1.15	0.602°
1.71	0.908°	2.33	1.180°
2.78	1.396°	3.64	1.774°
4.04	1.905°	5.07	2.383°
5.70	2.490°	6.65	2.998°
7.25	2.987°	7.79	3.444°
8.70	3.409°	9.46	4.060°
10.24	3.890°		
11.74	4.347°		
2 Para: 1 Ortho			
66.71 mol. % : 33.29 mol. %			
Mol. % compound	ΔT		
0.91	0.590°		
2.02	1.218°		
3.02	1.727°		
4.11	2.239°		
5.34	2.743°		
6.72	3.275°		
8.59	3.953°		

The freezing-point depression data for three of the systems (those for o-cresol, phenol and for an equimolecular mixture of phenol and o-cresol) are shown graphically in Figure III. The abnormally small depressions obtained for phenol show that this

substance is extensively associated. The curve for o-cresol, on the other hand, is very much closer to the ideal curve, indicating that it is much less associated than phenol. The equimolecular mixture gives a curve which falls practically midway between those of its two components. This indicates that the average molecular com-

plexity of the mixture is of the same order as that of the pure substances.

Exactly the same result is obtained from the other data given in Table VII above. Each of the two mixtures tested (phenol and m-cresol in molecular proportion 1 to 2; o-cresol and p-cresol in the molecular proportion 1 to 2) corresponds to a definite compound isolated by Dawson and Mountford. In each case the freezing-point depression curve for the compound mixture falls intermediate between the curves for the respective components, and nearer to that component in which the mixture is richer.

If these phenol-cresol compounds were true *addition* compounds (their formation involving an increase in molecular complexity) en-

tirely different results would have been obtained. Although the dissociation of such compounds into their simpler components would be favored by the dilution of the mixture with a large excess of solvent benzene we should still find appreciable combination indicated by abnormally small freezing-point depressions. Thus, to give an example, it has been found¹ that the freezing-point depression of a solution of ethyl acetate in benzene is practically unchanged on the addition of an equimolecular amount of trichloroacetic acid,² showing that the acid-ester addition compound formed is only slightly broken up into its components in benzene solution. Ethyl acetate and acetic acid give a similar, but much less decided increase in molecular complexity when mixed in benzene solution. In the system containing phenol and the cresols, however, the freezing-point depression curves resemble the viscosity curves in showing practically no change in molecular complexity; any compound formation between the components must therefore be compensated for by simultaneous depolymerization.

In order to supply a definite idea as to the relative molecular complexities in the different solutions examined, the following table is given. As an arbitrary concentration for comparing the different systems, 5 molecular per cent has been chosen. The added specific conductivity and viscosity data will be discussed later.

TABLE VIII

ASSOCIATION OF PHENOL, Etc., IN BENZENE SOLUTION

Solute concentration=5 molecular per cent.

	ΔT	Mol.Wt.	Avg Mol. Complex- ity	Spec.Cond. $\times 10^8$ at 25°	Viscosity at 25°
phenol	1.780°	178.4	1.897	8.84	0.08945
o-cresol	2.861°	125.1	1.157	0.127	0.07608
m-cresol	2.450°	146.9	1.358	1.397	0.1342
p-cresol	2.400°	150.2	1.390	1.378	0.1474
1 phenol+1 o-cresol ..	2.342°	144.5	1.427	0.979	0.08415
1 phenol+2 m-cresol ..	2.258°	153.2	1.482	2.230	0.1121
1 o-cresol+2 p-cresol..	2.613°	137.6	1.274	0.570	0.1177

The results given above are in good agreement with those of previous investigators³ in indicating that phenol is much more highly

¹Unpublished data obtained by Dr. J. E. Booge in this laboratory.

²Kendall and Booge, J.A.C.S., 38, 1712 (1916) show that the two substances form a stable equimolecular addition compound freezing at -27.5°.

³Beckmann, Z. physik. Chem., 2, 715 (1888); Aurvers, Ibid., 12, 689 (1893); Mascarelli and Benati, Gazz. chim. ital., 37, 527 (1907); 39 B, 642 (1909); Hewitt and Winmill, J. Chem. Soc., 91, 441 (1907).

associated than the cresols. The specific conductivity of phenol, it will be noted, is also considerably greater than the values obtained for the cresols—a fact in exact accordance with the work of Kendall and Gross² in which a parallelism between specific conductivity and molecular complexity in a series of liquids of similar type was predicted.

O-cresol is much less associated than its two isomers, for which the association factors, like their other physical properties, are quite similar. As was to be expected from their greater association the specific conductivities of m-cresol and p-cresol are much higher than that for o-cresol. The influence of this association factor is also evident in the relative viscosity values.

GENERAL CONCLUSIONS

The following experimental facts have been established with regard to phenol-cresol mixtures: (a) Dawson and Mountford have isolated compounds in five of the six possible binary systems by the freezing-point method, (b) the specific conductivity-composition curves show no significant divergence from the normal curves, (c) the viscosity-composition curves are all “pseudo-ideal” in type, (d) the freezing-depression curves (which are also relative molecular weight curves) given by binary mixtures in benzene solution fall intermediate between the curves found for the pure components. As noted above the conclusions drawn from these facts are not in harmony with one another. It now remains to be seen if a rational explanation can be given which will harmonize these results with the general hypothesis correlating chemical contrast, compound formation and conductivity in solution developed by Kendall and his co-workers, or whether the whole behavior of systems containing phenols must continue to be classed as “abnormal.”

A careful consideration of the problem shows that an extension to these solutions of the views presented by Kendall and Gross (loc. cit., p. . .) regarding conductivity and molecular complexity in pure associated liquids, and binary mixtures of the same, supplies a complete explanation of the points in dispute.

Phenol and the cresols, as already shown, are highly associated in the liquid state. The association of phenol, in particular, has been critically investigated by several investigators,¹ the conclusions

²Loc. cit.

¹Yamnaoto, Sakuri Memorial Papers, Article 12, p. 33 (1908); Mascarelli and Benati, loc. cit.; Beckmann and Maxim, Z. physik. Chem., 89, 411 (1914).

reached being that the main equilibrium is represented by the equation:

Some investigators² postulate the existence of still more complex molecular types of phenol.

Now it has been noted by Kendall and Gross that in a solution containing two highly associated components of similar character, compounds of the general type $(AB)_x \cdot (CD)_y$ are undoubtedly formed in quantity. The average molecular complexity of such a mixture, however, (and hence its specific conductivity also) will not differ greatly from that of its pure components since disassociation of these is also involved. The complexes here existent are to be regarded not as *addition* but rather as *substitution* compounds, for disintegration and recombination of the various molecular and ionic types present will finally result in an almost "haphazard" replacement of the different radicals by one another at all points of the original molecules (AB) and (CD) . If the attractive forces between the constituent groups are such that at a certain particular substitution complex is predominantly stable, then it is only logical to expect that such a complex may be definitely isolated under suitable conditions (e.g., by freezing the solution). The phenol-cresol compounds described by Dawson and Mountford are consequently not true *addition* compounds as the physical properties given above sufficiently demonstrate, but *substitution* compounds formed by the replacement of part of an associated molecule by part of a different associated molecule. It is very significant that all five of the compounds isolated by the freezing-point method are trimolecular, e.g., 2 m-cresol+1 phenol, 2 p-cresol+1 phenol. Such complexes could be readily formed from the predominating phenol complex $(\text{C}_6\text{H}_5\text{OH})_3$ by replacement of two phenol groups. No increase in the average molecular complexity of the mixture is involved in such replacements, and the apparent contradiction between Dawson and Mountford's results and those of the present work is therefore removed.

It must also be noted that mixtures of this type, if no particular substitution complex predominates in stability, will necessarily tend to give "mixed crystals" on solidification, as in the case of the phenol - o-cresol system. Analogous behavior is shown by binary

²Mascarelli and Benati, loc. cit.

mixtures of fused salts of similar character, e.g., neutral salts of the alkali metals.¹ Thus potassium sulfate gives a continuous series of solid solutions with sodium sulfate and also with potassium chromate. Lithium sulfate and potassium fluoride, on the other hand, form stable equimolecular compounds with potassium sulfate. These latter systems are evidently identical in character with the five compound-producing phenol-cresol mixtures.

SUMMARY

By repeated fractionation, very pure samples of phenol and the three cresols have been prepared, and their chief physical constants determined. The specific conductivity and viscosity curves for the different systems have been carefully determined. Freezing-point depression curves for phenol, the cresols, and various binary mixtures in benzene solution have also been constructed. Without exception, the results indicate that no increase in molecular complexity occurs in the different systems. This is in agreement with the views correlating addition compound formation with diversity in character of the components previously formulated by Kendall and his co-workers, but apparently in disagreement with the fact that in five of the six systems definite compounds were isolated by Dawson and Mountford.

A brief consideration of the equilibria existent in binary mixtures of associated liquids has shown that the compounds present in these systems are to be regarded as substitution rather than as addition compounds. Under this view the results of Dawson and Mountford and those of the present work fall directly into line with the general theory.

¹Landolt-Börnstein, Tabellen, 1912, p. 611-37.

VITA

Jacob J. Beaver was born in Schenectady, N.Y., on February 23, 1893, attending the grade and high schools of that city. He received the degree of B.S. from Union University in June, 1915. From September, 1915, until June, 1917, he attended the graduate school of Columbia University, receiving the degree of M.A. in June, 1916. From June, 1917, until he resumed his studies at Columbia he was in the government service. In 1919 he was laboratory assistant in physical chemistry, in 1920 Goldschmidt Fellow in Chemistry and in 1921 lecturer in chemistry in Columbia.

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